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Remarkable effect of organoaluminum activator on catalytic performance of bis(phenoxy-imine) titanium complexes in ethylene polymerization

Authors dedicate this work to Professor Maria Nowakowska, on her 80th birthday.

Summary — Three titanium complexes having phenoxy-imine chelate ligands: bis[*N*-(3,5-di-*tert*-butylsalicylidene)anilinato]titanium(IV) dichloride (complex I), bis[*N*-(3,5-di-*tert*-butylsalicylidene)-1-naphtylaminato]titanium(IV) dichloride (complex II) and bis[*N*-(salicylidene)-1-naphtylaminato]titanium(IV) dichloride (complex III) were synthesized and used as ethylene polymerization catalysts in conjunction with various organoaluminum compounds. It was found that both ligand structure and activator type (MAO, Et_3Al, Et_2AlCl, $EtAlCl_2$) had great impacts on activity of complexes investigated. On the other hand, the type of alkylaluminum compound, much more than the structure of the complex determines the properties of products of the polymerization leading to high molecular weight polyethylene or low molecular weight polyethylene and oligomers.

Key words: ethylene polymerization, post-metallocene catalyst, phenoxy-imine ligand, FI catalyst.

WPŁYW GLINOORGANICZNEGO AKTYWATORA NA WŁAŚCIWOŚCI KATALITYCZNE BIS(FENOKSY-IMINOWYCH) KOMPLEKSÓW TYTANU W POLIMERYZACJI ETYLENU

Streszczenie — Zsyntezowano i sprawdzono w polimeryzacji etylenu, po uprzedniej aktywacji zarówno MAO, jak i prostymi związkami glinoorganicznymi (Et_3Al, Et_2AlCl, $EtAlCl_2$), trzy kompleksy tytanu z ligandami fenoksy-iminowymi: dichlorek bis[*N*-(3,5-di-*tert*-butylosalicylideno)anilino]tytanu(IV) (kompleks I), dichlorek bis[*N*-(3,5-di-*tert*-butylosalicylideno)-1-naftyloamino]tytanu(IV) (kompleks II) i dichlorek bis[*N*-(salicylideno)-1-naftyloamino]tytanu(IV) (kompleks III). Stwierdzono, że zarówno struktura ligandów, jak i rodzaj glinoorganicznego aktywatora mają wpływ na aktywność badanych kompleksów. Kompleks I, zawierający podstawnik fenylowy przy iminowym atomie azotu okazał się najaktywniejszy w połączeniu z MAO, zaś kompleksy II i III, zawierające w tej pozycji podstawnik naftylowy, okazały się dużo aktywniejsze po aktywacji $EtAlCl_2$ lub Et_2AlCl (rys. 2). Ponadto zauważono, że rodzaj glinoorganicznego aktywatora, w przeciwieństwie do struktury liganda, wpływa na właściwości otrzymanych produktów (tabela 1). W procesach polimeryzacji, w których w charakterze aktywatora zastosowano MAO lub Et_3Al zawsze powstawał liniowy polietylen o wysokiej temperaturze topnienia z zakresu 126,4—138,3 °C. W reakcjach prowadzonych w takich samych warunkach, wobec tych samych kompleksów, ale aktywowanych prostymi związkami glinoorganicznymi zawierającymi atom chlorowca, otrzymywano stały produkt o niskiej masie molowej i oligomery.

Słowa kluczowe: polimeryzacja etylenu, katalizator postmetalocenowy, ligand fenoksy-iminowy, katalizator FI.

At the beginning of the nineties of the twentieth century the development of the newest generation of catalysts for polymerization of olefins called postmetallocene systems was initiated. Mainly the structures of ligands in these catalysts make them different from the catalysts of previous generations. They contain highly steric mono-, di-, tri- or tetradentate ligands. In recent years the complexes containing bidentate ligands, among which phenoxy-imine ligands dominate considerably, have aroused particular scientific interest. In the complexes containing ligands of this kind most frequently the atom of zirconium [1—9] or less frequently the atom of titanium appear to be a metallic centre [2, 4—6, 8—14], like in metallocene catalysts. Less attention is drawn to hafnium [4, 5] or vanadium complexes [8]. There are also known late transition metal complexes with fenoxy-imine ligands for ethylene oligomerization [15].

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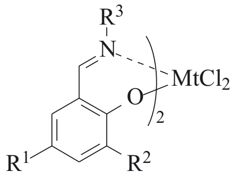
Early transition metal bis(phenoxy-imine) complexes, which were named FI catalysts [general structure is presented as formula (I)], appeared to be active catalysts not only for ethylene and propylene but also for higher 1-olefins polymerizations [13]. Comparison of activity of the zirconium complex of this kind and a typical metallocene one (Cp_2ZrCl_2) in ethylene polymerization carried out under identical conditions proved that FI catalysts may exhibit even higher activity than metallocene catalyst [3]. Moreover, apart from their high activity FI catalysts can be characterized by an ability to form polymers with unique qualities, *e.g.* low-density and linear low-density polyethylenes, isotactic and syndiotactic polypropylenes, syndiotactic polystyrene [6], or regio- and steroirregular high molecular weight poly(1-hexane)s [2]. Furthermore, such complexes can be used in the syntheses of ethylene/propylene, ethylene/1-butene or ethylene/norbornene as well as di- or multiblock copolymers [2, 10]. Fluorinated bis(phenoxy-imine) titanium complexes show particular properties. They catalyze living ethylene [5, 13, 16] and propylene polymerizations [5, 12] and their copolymerizations [10].



(I)

Mt = transition metal (Ti, V, Zr, Hf)

R^1, R^2, R^3 = substituent

It was affirmed in a number of works on catalysts containing phenoxy-imine ligands that the efficiency of (co)polymerization and the properties of the products obtained depended on catalytic system composition, *e.g.* metal type, structure of ligands and the kind of organoaluminum activator used.

Thus, the results presented in [4] showed that the type of metal centre (Ti, Zr, Hf) in bis(phenoxy-imine) complexes demonstrates essential effect on ethylene polymerization productivity. Among the three described complexes, the zirconium complex showed the highest activity [519 $kg_{PE}/(mmol_{cat.} \cdot h)$] and the activities of titanium and hafnium ones were significantly lower [3.3 $kg_{PE}/(mmol_{cat.} \cdot h)$ and 6.5 $kg_{PE}/(mmol_{cat.} \cdot h)$, respectively].

In the literature much more attention is devoted to research on influence of phenoxy-imine ligands structures on activity of the resulting complex. For example, in the work [6] the influence of R^2 substituent [formula (I)] on activity of examined complexes and the influence of R^3 substituent on the molecular weight of obtained polyethylene (PE) were tested. It was demonstrated that the introduction of bulky alkyl substituents R^2 led to the higher activities of the tested catalysts and that the presence of a bulky alkyl group at *ortho* position in the phenyl group at R^3 position led to higher molecular weight of the products obtained [6].

Methylalumoxane (MAO) is usually used as an activator of bis(phenoxy-imine) complexes [2—8, 10—14], however in work [1] the usefulness of other organoaluminum compounds as activators for zirconium complexes was tested. Studies were performed for bis[*N*-(3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride and bis[*N*-(3-*tert*-butylsalicylidene)cyclohexylaminato]zirconium(IV) dichloride activated with the following organoaluminum compounds: Et_3Al, He_3Al, Me_3Al, *i*-Bu_3Al, Et_2AlCl, MAO. It was found that the efficiency of activators for the first complex was decreasing in the order: MAO > Et_3Al > Me_3Al >> He_3Al (for *i*-Bu_3Al and Et_2AlCl no product was obtained). On the other hand, the efficiency of the second complex was changing in the following way: Et_3Al > He_3Al >> Me_3Al [1].

It is to be stressed that similar research on the influence of the kind of organoaluminum activator on the activity of complexes of other metals with phenoxy-imine ligands is not reported in the literature. Furthermore, it is known that commonly used MAO is a chemical compound with non-defined structure and very expensive. Therefore, it would be advantageous to replace it with a cheaper organoaluminum compound of defined structure. It seemed therefore advisable to examine the effectiveness of common organoaluminum compounds as activators of bis(phenoxy-imine) titanium complexes in ethylene polymerization. Especially, that the results of our earlier work involving titanium complexes with tetradentate ligands [O, N, N, O] showed that these complexes were active in combination with both MAO or Et_2AlCl. Moreover, we found that the properties of the product obtained differed dependently on an activator used. Linear polyethylene having high molecular weight (of the order of a few hundred thousand) was formed in the presence of MAO; polyethylene having low molecular weight (the order of a few thousand) as well as oligomers were obtained when Et_2AlCl was an activator [17].

In this paper the effects of the type and concentration (Al/Ti molar ratio) of organoaluminum activator for bis(phenoxy-imine) titanium complexes on their productivity in ethylene polymerization and properties of the polymer obtained were demonstrated. In the study three titanium complexes which have not been examined so far and differing in a type of R^3 group at imine nitrogen and substituents in the phenolate rings were used. Some alkylaluminum compounds, such as MAO, Et_3Al, Et_2AlCl, $EtAlCl_2$ were used as activators.

EXPERIMENTAL

Materials

All manipulations during complex and PE syntheses were carried out in oxygen-free conditions using inert (nitrogen or argon) atmosphere and the standard Schlenk and glove box techniques. Ethylene 3.0 (Linde Gaz Polska), nitrogen (Messer) and argon (Linde Gaz Polska) were used after having been passed through a column with sodium metal supported on Al_2O_3.

CH_2Cl_2 and toluene (POCh) were distilled from calcium hydride and sodium, respectively, before use.

Methylalumoxane (MAO) (10.0 wt. %, Aldrich), Et_3Al (25 wt. %, Aldrich), Et_2AlCl (1.0 M, Aldrich) and $EtAlCl_2$ (25 wt. %, Aldrich), $TiCl_4$ (Aldrich) were used without further purification.

Phenoxy-imine ligands were synthesized in reactions of salicylaldehyde or 3,5-di-*tert*-butylsalicylaldehyde with a primary amine compound *via* Schiff base condensation in ethanol as it was described in [3]. The syntheses were carried out by the research team of Professor W. Bukowski (Rzeszow Technical University).

Syntheses of Ti complexes

A typical procedure for a complexation is as follows: to a stirred solution of $TiCl_4$ (3.9 mmol) in dichloromethane (25 cm^3) a solution of phenoxy-imine ligand (7.8 mmol) in 25 cm^3 of dichloromethane was added dropwise over a 30 min period. The resulting mixture was stirred for 24 hours at room temperature, and then the solvent was evaporated. The obtained solid product was washed with hexane and then dried under argon, and finally under vacuum.

Polymerization reaction

Ethylene polymerization was carried out in 500 cm^3 glass reactor equipped with a stirrer and heating-cooling jacket. First, the solvent (150 cm^3 of toluene), then the activator and the complex solution in toluene were added to the reactor. After the catalyst injection ethylene was added and its pressure was maintained at 0.5 MPa during polymerization. The reaction was carried out for 30 minutes and then was quenched by addition of a dilute solution of hydrochloric acid in methanol. The polymer obtained was filtrated, washed with methanol and dried under vacuum.

Methods of testing

Polymer melting temperature (T_m) and crystallinity (*C*) were determined by differential scanning calorimetry (DSC) using a 2010 DSC calorimeter from TA Instruments. A second heating cycle was used for collecting of DSC thermogram data.

Molecular weight (M_w) values and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography (GPC) at 135 °C, with the use of 1,2,4-trichlorobenzene (TCB) as a solvent and polystyrene standards as the reference.

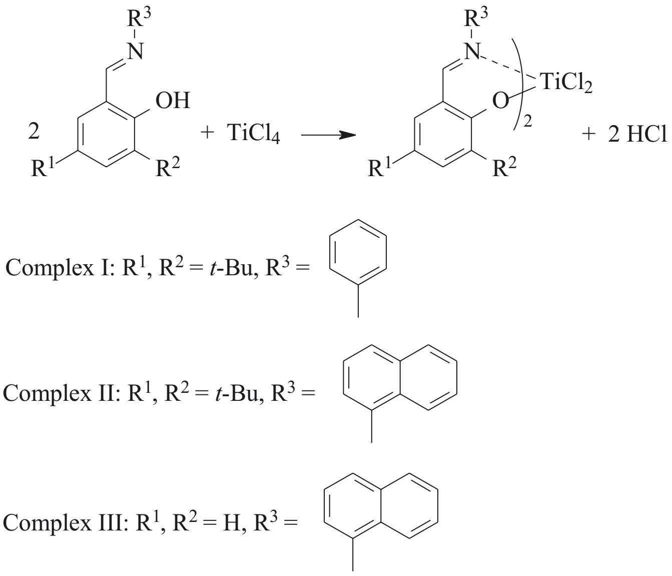
IR analyses of complexes were performed with the use of Nicole Nexus, 2002 FT-IR spectrometer.

RESULTS AND DISCUSSION

Complexes syntheses

Within the framework of this research three bis(phenoxy-imine) titanium complexes were synthesized: bis-[*N*-(3,5-di-*tert*-butylsalicylidene)anilinato]titanium(IV) dichloride (complex I), bis[*N*-(3,5-di-*tert*-butylsalicylidene)-1-naphthylaminato]titanium(IV) dichloride (complex II) and bis[*N*-(salicylidene)-1-naphthylaminato]titanium(IV) dichloride (complex III). These complexes varied in the kinds of substituents at imine nitrogen (R^3 substituent). Namely, complex I has a phenyl group in this position and complexes II and III have naphthyl groups. These complexes also vary in the kinds of substituents in phenolate rings; that is, complexes I and II have *tert*-butyl groups at R^1 and R^2 positions while complex III has hydrogen atoms there.

The syntheses of bis(phenoxy-imine) complexes were carried out in ethylene dichloride at ambient temperature. In this reaction a ligand with an appropriate struc-



Scheme A. Reaction of a complex synthesis

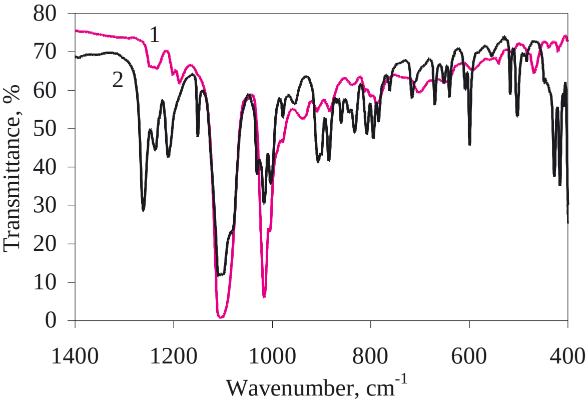


Fig. 1. FT-IR spectra of complex II (1) and corresponding ligand (2)

ture reacted with titanium tetrachloride in 2:1 molar ratio (Scheme A). All complexes were obtained with good productivities within the 74—97 % range. Complexes I and II were brown while complex III had a maroon tint. In FT-IR spectra of complexes obtained one can see the band coming from stretching vibrations of C=N groups and this band is shifted towards lower wave numbers in the spectrum of the complex as compared to the ligand's spectrum. These shifts are connected with the change in electron density caused by the presence of electron acceptor, most probably a titanium atom. Figure 1 shows the examples of spectra obtained for complex II and its corresponding ligand.

Ethylene polymerization

Influence of activator type and ligand structure

All synthesized titanium complexes, after activation with alkylaluminum compound, were used in ethylene polymerization. MAO and common alkylaluminum compound such as Et_3Al, Et_2AlCl or $EtAlCl_2$, were applied and the process of polymerization was carried out under constant conditions *i.e.* in toluene, at 50 °C, under 0.5 MPa of ethylene and for 30 min. The used activator-complex molar ratio was equal to 100:1 unless indicated otherwise. The results obtained are presented in Figure 2.

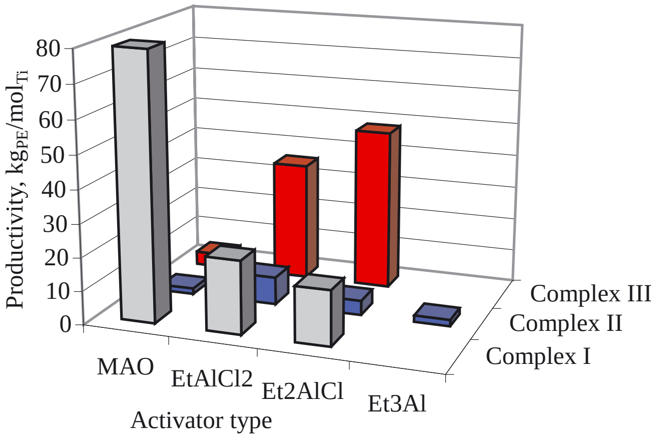


Fig. 2. Effects of activator type and ligand structure on ethylene polymerization productivity; polymerization conditions: [Ti] = 0.08 mmol, [Al] = 8 mmol

As can be seen, the catalyst productivity considerably depends on both ligand structure in a complex and the kind of organoaluminum activator. Complex I containing phenyl group attached to imine nitrogen atom (R^3 substituent) and *tert*-butyl groups in the phenolate ring (R^1 and R^2 substituent) appeared to be the most active one in conjunction with MAO, a typical activator for bis(phenoxy-imine) complexes [2—8, 10—14]. This catalytic system gives PE with productivity of 79.7 $kg_{PE}/mol_{cat.}$. However, it is to be stressed that this complex is also active in conjunction with common alkylaluminum compounds which have not so far been applied as activators for bis(phenoxy-imine) titanium complexes. The values of productivity of the polymerization processes carried out in the presence of these activators are lower, though. The productivity of complex I activated with $EtAlCl_2$ did not exceed 22 $kg_{PE}/mol_{cat.}$ and if Et_2AlCl was used as an activator, catalyst productivity was 16.5 $kg_{PE}/mol_{cat.}$.

Unlike complex I the two complexes containing naphthyl group at R^3 position and *tert*-butyl groups or hydrogen atoms at R^1 and R^2 positions (complexes II and III, respectively) are considerably more active if common organoaluminum compounds are used as activators instead of MAO. Catalytic system complex II/$EtAlCl_2$ appeared to be almost five times more active than the complex II/MAO (8.3 $kg_{PE}/mol_{cat.}$ and 1.7 $kg_{PE}/mol_{cat.}$, respectively); complex III is about ten times more active if Et_2AlCl is used as an activator, not MAO (48.2 $kg_{PE}/mol_{cat.}$ and 4.1 $kg_{PE}/mol_{cat.}$, respectively).

Additionally, the efficiency of polymerization for complex II with Et_3Al as an activator was examined. It was found that the activity of such system is insignificant and close to the activity of the complex activated with MAO. These results show that common alkylaluminum compounds with chlorine atoms are more advantageous activators of complexes containing naphthyl group at the imine nitrogen atom.

As it was mentioned earlier the structure of ligand also influences the activity of examined complex. By comparing the activity of complexes I and II in which R^3 substituent is different (phenyl and naphthyl group, respectively) it can be seen (Fig. 2) that complex I containing phenyl group is considerably more active regardless of the organoaluminum compound used.

On the other hand, from among the complexes in which the substituents were different in the phenolate ring, *i.e.* containing *tert*-butyl groups or hydrogen atoms at R^1 and R^2 positions (complexes II and III, respectively), the complex which did not contain bulky *tert*-butyl groups appeared to be more active. Such influence of the substituent in complexes on the productivity of the polymerization process is observed irrespective of organoaluminum activator applied.

Influence of Al/Ti molar ratio

Subject related literature sources say that transition metal complexes with phenoxy-imine ligands are usually activated with an excessive amount of organoaluminum compound in relation to the complex. The amounts of both components in the catalytic system expressed as Al/Ti molar ratio usually include a value from the scope of a few thousand to a dozen or so thousand. The results presented so far in this paper were obtained using a relatively low activator-complex molar ratio (100:1) in the polymerization process, which clarifies the unsatisfactory quantity of obtained polymerization productivities. Therefore, it was decided to check

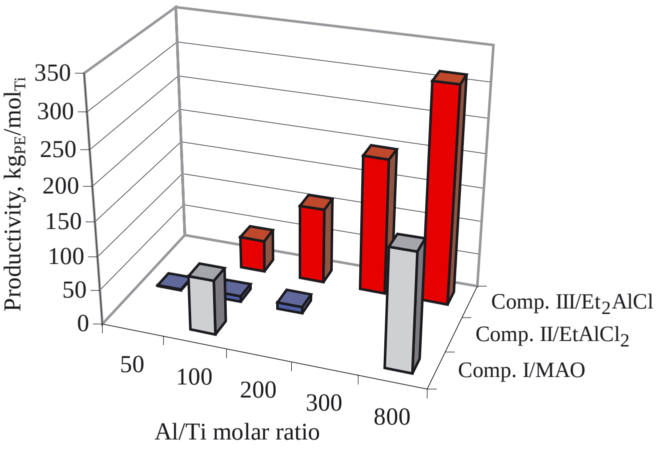


Fig. 3. Effect of Al/Ti molar ratio on catalyst productivity; polymerization conditions: [Ti] = 0.08 mmol

the effect of molar ratio on catalyst productivity. The research was done for the three selected catalytic systems which have so far been the best ones: complex I/MAO, complex II/$EtAlCl_2$ and complex III/Et_2AlCl. Results are presented in Figure 3.

As can be seen, the increase in molar ratio of activator and the complex always causes the increase in activity of catalytic systems tested regardless of their compositions. The greatest (almost seven-fold) increase in catalyst productivity along with an increase in Al/Ti molar ratio from 100 to 800 was reached in case of catalyst complex III/Et_2AlCl. One can even expect that further increase in amount of activator, usually up to its optimum value which is typical for each catalytic system, will cause further increase in activity of the catalyst. For example, the optimum value for a system bis[*N*-3-*tert*-butylsalicylidene)anilinato]zirconium(IV) dichloride/Et_3Al amounts to 15 000:1 mol/mol [1].

Polymer properties

Determination of T_m, C, M_w and M_w/M_n of ethylene polymerization products showed that the structures of complexes influence to a lower degree the properties of the products obtained than the type of organoaluminum activator used (Table 1).

PE formed in the presence of complexes I and III activated by MAO has a high T_m value about 138 °C, and a high degree of C (over 75 %) (Table 1, entries 1 and 8). PE obtained with use of the complex II activated with Et_3Al (Table 1, entry 7) exhibits similar properties, high T_m and degree of C. Complex II in conjunction with MAO gives PE with lower T_m equal to 126.4 °C and C 84.9 %.

The differences in T_m of polymers synthesized with complexes I and III as well as PE obtained with complex II result from their different M_w values. As can be seen in Table 1 (entry 1) in the presence of catalyst complex I/MAO, PE with high M_w about 400 000 and broad M_w/M_n (15.6) is produced. A product with a much lower M_w (about 30 000) is formed in the presence of a catalyst containing complex II. It should be stressed, however, that chromatogram exhibits an additional peak which corresponds to the fraction of polymer with higher M_w. The peak is difficult to interpret, though.

Table 1. Effect of catalyst composition on selected properties of polymerization products

Entry	Complex	Activator	T_m, °C	C, %	M_w	M_w/M_n
1	I	MAO	137.8	75.6	401 900	15.6
2	I	$EtAlCl_2$	109.4, 118.5, 121.4	—	nd*)	nd*)
3	I	Et_2AlCl	105.0, 120.6	—	4700	1.5
4	II	MAO	126.4	84.9	27 900	1.3
5	II	$EtAlCl_2$	70.0, 107.2, 116.1	—	5100	1.5
6	II	Et_2AlCl	102.3	—	5000	1.2
7	II	Et_3Al	136.8	80.4	nd*)	nd*)
8	III	MAO	138.3	75.4	nd*)	nd*)
9	III	$EtAlCl_2$	109.4, 120.5, 122.5	—	nd*)	nd*)
10	III	Et_2AlCl	106.5, 121.5	—	7200	1.5

*) nd — not determined.

The same complexes in conjunction with common organoaluminum compounds containing an atom of a halogen ($EtAlCl_2$ or Et_2AlCl) form the products showing completely different properties (Table 1, entries 2, 3, 5, 6, 9 and 10). DSC curves show the presence of several minima differing from each other even by a few dozen degrees, but not exceeding 123 °C. Figure 4 shows a few

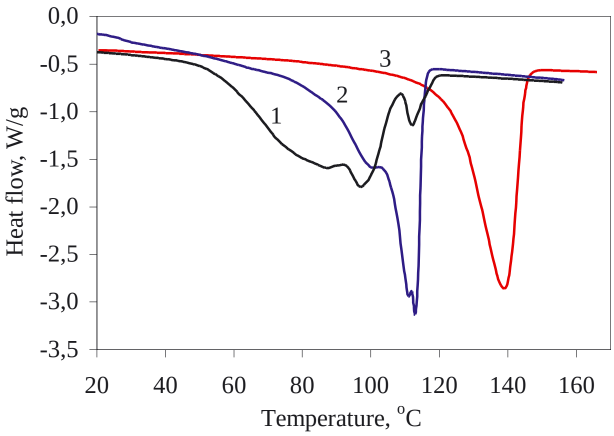


Fig. 4. Thermograms of polyethylene obtained with use of the complex II activated with: 1 — Et_2AlCl, 2 — $EtAlCl_2$, 3 — MAO

examples of thermograms of polymers obtained with use of a complex II activated with different organoaluminum compounds.

Determinations of molecular weights showed that the polymers synthesized with complexes I, II and III activated with Et_2AlCl can be characterized by low M_w value of the order of a few thousand (Table 1, entries 3, 6 and 10). Furthermore, their chromatograms exhibited a peak coming from considerably higher M_w, yet their value cannot be estimated unambiguously. As it was in case of polymer produced with complex II/$EtAlCl_2$ (Table 1, entry 5) for which the peaks corresponding to low and high M_w can be observed, in case of low M_w, M_w/M_n exhibited a significant bimodality. It was checked if additional oligomers were formed since the solid products of polymerizations obtained with use of complexes activated with chlorinated organoaluminum compounds had low M_w. Indeed, in post-reaction liquid mixture the presence of oligomers containing from a few to a few dozen atoms of carbon in a molecule was confirmed. The atoms were always even numbered.

Table 2. Effect of Al/Ti molar ratio on selected properties of polymerization products

Entry	Complex	Activator	Al/Ti molar ratio	T_m, °C	C, %	M_w	M_w/M_n
1	I	MAO	100	137.8	75.6	401 900	15.6
16	I	MAO	800	138.7	62.1	929 800	15.7
11	II	$EtAlCl_2$	50	81.8, 116.3	—	nd*)	nd*)
5	II	$EtAlCl_2$	100	70.0, 107.2, 116.1	—	5100	1.5
12	II	$EtAlCl_2$	200	106.9, 115.5	—	nd*)	nd*)
10	III	Et_2AlCl	100	106.5, 121.5	—	7200	1.5
13	III	Et_2AlCl	200	93.8, 107.3, 119.0	—	4700	1.3
14	III	Et_2AlCl	300	109.0, 113.7, 121.2	—	5800	1.5
15	III	Et_2AlCl	800	107.8, 120.8	—	5300	1.5

*) nd — not determined.

Furthermore, it should be noted that similar results concerning influence of type of organoaluminum activator on the properties of polymers obtained are gained regardless of Al/Ti molar ratio. As it can be seen in Table 2, polyethylene produced in the presence of a complex I activated with MAO at Al/Ti molar ratio equal to 100 and 800 shows high T_m (over 137 °C), high M_w value (few hundred thousand) and broad M_w/M_n (about 15). On the other hand, when common alkylaluminum compounds ($EtAlCl_2$ or Et_2AlCl) were used as activators for complexes II and III at different molar ratios, PE obtained always had low M_w (about few thousand), which decreased with increasing Al/Ti molar ratio.

CONCLUSION

In this study we demonstrated that organoaluminum activator had remarkable effects on both activity of bis(phenoxy-imine) titanium complexes and on properties of the products obtained while the structure of complex influences first and foremost its activity in the polymerization process. Complex I containing phenyl substituent at R^3 position appeared to be the most active one in conjunction with MAO. Complexes II and III containing in turn naphthyl substituent at R^3 position are more active in conjunction with common organoaluminum compounds containing halogen atoms (Et_2AlCl, $EtAlCl_2$). It was also found that PE with high T_m was always formed regardless of the structure of ligand in the presence of MAO and Et_3Al as activator. The use of an organoaluminum compound containing a halogen atom as a activator leads to the formation of mixture of oligomers and polyethylene with low M_w value of the order of a few thousand (with an admixture of a small quantity of fraction having considerably higher M_w).

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W kolejnym zeszycie ukażą się m.in. następujące artykuły:

- *A. A. A. Rashdi, S. M. Sapuan, M. M. H. M. Ahmad, A. Khalina* — Kompozyty polimerowe wzmacniane włóknami kenafu — przegląd literatury (*j. ang.*)
- *J. Kucińska-Lipka, H. Janik, A. Balas* — Synteza, budowa chemiczna i właściwości sieciowanych styrenem poli(estro-eterouretanów) otrzymanych z nienasyconych oligo(alkilenoestro-etero)dioli i 4,4′-diizocyjanianu difenylometanu
- *A. Mija, C. N. Cascaval* — Ciekłokrystaliczne termoutwardzalne materiały epoksydowe z azometinową grupą mezogeniczną
- *V. Rabová* — Badania struktury oraz reologicznych i mechanicznych właściwości nanokompozytów kauczuk silikonowy/montmorylonit (*j. ang.*)
- *I. Neamtu, L. E. Nita, M. Bercea, A. P. Chiriac* — Właściwości reologiczne chemicznie usieciowanych hydrożeli na podstawie poli(akryloamidu) (*j. ang.*)
- *M. Jastrzębska, M. Rutkowska, H. Janik, S. Jose, S. Thomas* — Morfologia i właściwości mechaniczne recyklatu z laminatu polietylen/poliamid 6 (*j. ang.*)
- *N. Tudorachi, A. P. Chiriac* — Biodegradowalna matryca polimerowa i magnetyczne kompozyty na jej podstawie
- *M. Przybyszewska, M. Zaborski, A. Masek* — Koagenty sieciowania nadtlenkowego uwodornionego elastomeru butadienowo-akrylonitrylowego
- *S. Borysiak, B. Doczekalska* — Wpływ chemicznej modyfikacji drewna na jego aktywność nukleacyjną w kompozytach z polipropylenem (*j. ang.*)
- *Z. Czech, R. Pełech* — Degradacja termiczna akrylanowych klejów samoprzylepnych na bazie kopolimerów z akrylanu 2-etyloheksylu oraz kwasu akrylowego (*j. ang.*)
- *P. Rybiński, G. Janowska* — Wpływ dodatku antypirenów na stabilność termiczną i palność usieciowanych kauczuków nitrylowych
- *A. Bieniek, B. Lipp-Symonowicz, S. Sztajnowski* — Wpływ struktury włókien z poliamidu 6 na przebieg ich starzenia w warunkach silnego nasłonecznienia (*j. ang.*)